DEVELOPMENT OF PVDF/PEG THIN FILM COMPOSITE MEMBRANE FOR CO_2/N_2 GAS SEPARATION

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ABSTRACT

This research study develops polyvinylidenefluoride-poly ethylene glycol (PVDF/PEG) thin film composite (TFC) membrane for CO_2/N_2 gas separation. Asymmetric thin flat sheet membrane was prepared by dry wet phase inversion process consisting 15 %w/v of (PVDF) as the support layer polymer, 82 %w/v of N-methyl-2-pyrrolidone (NMP) as the solvent and 3 %w/v of distilled water as the non-solvent. Different concentration of poly (ethylene glycol) (PEG) polymer acts as the top film was study with 10 %, 15%, and 20% by using dip-coating method. The morphological structures of produced membranes were examined using Scanning Electron Microscopy (SEM). The Fourier Infrared Spectroscopy (FTIR) analysis also conducted in order to characterize the existence of the chemical bonding type in the membrane. The performance of the membrane was examined by conducting the gas permeation test. Pure carbon Dioxide (CO_2) and pure nitrogen (N_2) were used as the test gases by using feed ration range from 0.5 to 1.5 bars. As expected by the morphological structure, 10% PVDF/PEG (TFC) membrane showed the best performance compared to 15% and 20% PVDF/PEG TFC membrane. The selectivity of CO_2/N_2 was (1.01 at 0.5 bar), (1.07 at 1.0 bar) and (1.08 at 1.5 bar) for 20% PVDF/PEG TFC membrane, (1.02 at 0.5 bar), (1.11 at 1.0 bar) and (1.22 at 1.5 bar) for 15% PVDF/PEG TFC membrane, (1.03 at 0.5 bar), (1.27 at 1.0 bar), (1.43 at 1.5 bar) for 10% PVDF/PEG TFC membrane. From the investigation, PVDF/PEG (TFC) membrane was pointed the higher performance of selectivity and permeability behavior and hereby supposedly selected for future membrane development. The concentration of top layer membrane was discovered to affect the morphological structure which will preferentially affect the performance of the PVDF/PEG TFC membrane. Therefore, from the study conducted the most suitable asymmetric (TFC) membrane to developed high performance with concentration in range of 10% PVDF/PEG TFC membrane.

PENGHASILAN PVDF/PEG KOMPOSIT NIPIS MEMBRAN UNTUK PEMISAHAN CO_2/N_2 GAS

ABSTRAK

Penyelidikan ini adalah untuk menghasilkan fluoride polyvinylidene-polietilena glikol (PVDF/PEG) filem nipis komposit (TFC) membran untuk CO_2/N_2 pemisahan gas. Asimetrik nipis lembaran rata membran telah disediakan oleh fasa kering/basah inversi yang terdiri daripada 15% w/v (PVDF) sebagai sokongan lapisan polimer, 82% w/v N-metil-2-pyrrolidone (NMP) sebagai pelarut dan 3% w/v air suling sebagai bukan pelarut. Kepekatan (PEG) polimer yang berbeza bertindak sebagai filem atas adalah kajian bagi 10%, 15%, dan 20% dengan menggunakan celup kaedah salutan. Struktur morfologi membran yang dihasilkan telah diuji dengan menggunakan Pengimbas Mikroskop Electron (SEM). Fourier Transform Spektroskopi Inframerah (FTIR) juga dilakukan untuk mengesan kewujudan jenis ikatan kimia dalam membran. Prestasi membran telah diperiksa dengan menjalankan ujian penyerapan gas. Karbon dioksida (CO_2) dan nitrogen (N_2) telah digunakan sebagai gas ujian dengan menggunakan pelbagai tekanan dengan 0.5 hingga 1.5 bar. Seperti yang dijangka oleh struktur morfologi, 10% PVDF/PEG (TFC) membran menunjukkan prestasi yang terbaik berbanding dengan 15% dan 20% PVDF/PEG TFC membran. Kepilihan CO_2/N_2 adalah (1.01 pada 0.5 bar), (1.07 pada 1.0 bar) dan (1.08 pada 1.5 bar) untuk 20% PVDF/PEG TFC membran, (1.02 pada 0.5 bar), (1.11 pada 1.0 bar) dan (1.22 pada 1.5 bar) untuk 15% PVDF/PEG TFC membran, (1.03 pada 0.5 bar), (1.27 pada 1.0 bar), (1.43 pada 1.5 bar) 10% PVDF/PEG TFC membran. Mengikut kajian yang dijalankan, PVDF/PEG (TFC) membran telah menunjukkan prestasi yang lebih tinggi ketelapan pemilihan ini dipilih untuk penghasilan membran pada masa akan datang. Kepekatan membran lapisan atas telah dikesan boleh menjejaskan struktur morfologi terutamanya.menjejaskan prestasi PVDF/PEG filem nipis komposit membran. Dengan itu, daripada kajian yang dijalankan, asimetrik (TFC) membran yang paling sesuai dan berpontensi tinggi adalah konsentrasi 10% PVDF/PEG filem nipis komposit membrane.

TABLE OF CONTENTS

2 LITERATURE REVIEW

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CO_2	-	Carbon Dioxide
N_2	-	Nitrogen
TFC	-	Thin Film Composite
PEG	-	Polyethylene Glycol
PVDF	-	Polyvinylidenefluoride
SEM	-	Scanning Electron Microscopy
FTIR	-	Fourier Transform Infrared Ray
wt	-	Weight
v	-	Volume
V	-	Volume
P	-	Permeance
Q	-	Flow Rate
l	-	Thickness of Membrane
ΔP	-	Trans-membrane Pressure
T	-	Time Displacement
A	-	Effectiveness Membrane Area
NMP	-	N-Methyl-1-Pyrrolidone
α	-	Selectivity
IR	-	Infrared Ray
Pj	-	Permeability of another Gas Component
Pi	-	Permeability of One Gas Component

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

Gas separation by applying membrane technology plays an important role in minimizing the environmental impacts and cost for industrial processes specifically. According to Freeman (2005) at the moment, the most widely used membrane materials for gas separation are polymers. The economics of a gas separation membrane process is widely determined by the membrane's transport properties. Ideally, membranes should exhibit high selectivity and high permeability. Each gas component in a feed mixture has a characteristic permeation rate through the membrane. The rate is determined by the ability of the component to dissolve in and diffuse through the membrane material.

Recently, separation of carbon-dioxide from power plant flue gas and sequestration as liquid carbon dioxide into salt domes is a target of research programs around the world. The uses of selective membranes to separate carbon dioxide from flue gas have been suggested. The design process uses membranes with very high permeance and selectivity. Very low cost membrane and membrane modules are needed to make this process viable (Driolli, 2009).

Currently, development of thin film composite (TFC) membrane is one of the advance trends in material development for better gas separation membrane performance. Thin film composite (TFC) gas separation membranes useful in the separation of oxygen, nitrogen, hydrogen, water vapor, methane, carbon dioxide, hydrogen sulfide, lower hydrocarbons, and other gases are disclosed. Synthesis of membrane is one of the interesting parts. The most technically used membrane is made from organic polymer via phase separation methods. The phase-inversion process consists of the induction of phase separation in a previously homogeneous polymer solution either by temperature change, by immersing the solution in a non solvent bath (wet process) or exposing it to a non-solvent atmosphere (dry process) (Driolli, 2009).

1.2 Problem statement

The progress in the field of gas separation was grown mostly through the basic concepts of solution-diffusion implementation. The factor of membrane performance variables are selectivity and permeability. In gas separation, membrane selectivity is utilized to match up to the separating capability of a membrane for two or more species. Usually, the relationship between these aspects of membrane performance is directly proportional to each other; high selectivity membranes have more permeability and vice versa. Membrane application driven by development of gas separation technology has some problems that must be solved before commercially use. One of the major problems related in gas separation processes is the better membrane are required to change market economics significantly. Therefore, by developing (TFC) membrane is in order to provide good separating characteristics and mechanical strength rather than relying upon a single polymer membrane in improving the gas separation performance. This is the major study need to approach in this field to make the membrane capable in expanding what market significantly required.

1.3 Objective of Research

Based on the problem statement described in the previous section, the following were the objectives of this research:

1) To synthesis thin film composite (TFC) membrane.
2) To test the performance of thin film composite (TFC) membrane.
3) To analysis the physical and chemical properties of (TFC) membrane.

1.4 Scopes of the Study

In this research, there are several scopes of the study in order to achieve the above objective mentioned which are:

1) Synthesizing (TFC) membrane from PVDF as a support by using dry/wet phase inversion.

2) Conducting an experiment to study on (TFC) membrane performance using single gas permeation test.
3) Characterizing the membranes morphology by using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Ray (FTIR).

1.5 Rationale and Significant

The higher selectivity of membrane is the target of membrane separation process. Thus, the synthesis of (PVDF/PEG) thin film composite (TFC) membrane is one of the ways to enhance the membrane performance for gas separation process to be economically and effectively driven to the advance development applicable and reliable nowadays.

- In term of productivity and membrane performance:

✓ This research has been done to test the performance of (TFC) membrane. The better distribution of thin film permeability behavior towards carbon dioxide and nitrogen gas through the membrane increased the selectivity of the gas separation. Flat asymmetric thin film composite membrane exhibited highly selectivity than plain membrane based on the characterization of (TFC) membrane performance by using Scanning Electron Microscopy (SEM) device which analyzed the morphology of the (TFC) membrane, permeation test which demonstrated the permeability and selectivity performance and chemical and physical properties of (TFC) membrane by using Fourier Transform Infrared Ray (FTIR) accordingly.

- In term of economical aspect:

- ✓ The cost is significantly lower than the polymer replacement and energy cost associated with traditional technologies. The improvement in developing membrane and pretreatment design contribute a longer useful membrane life, which further recovers operating costs.

- In term of environmental aspect:
- ✓ Membrane systems do not involve the periodic removal and handling of spent solvents or polymers. Instead of that, incinerationn process can be performed for the items which do not require proceeding through disposal process.

CHAPTER 2

LITERATURE REVIEW

2.1 Definition and Development of Membrane

A Membrane is a selective barrier that allows the separation of certain species in a fluid by combination of separating and sorption diffusion mechanism. Separation is achieved by selectively permeating one or more components of a stream through the membrane while avoiding the passage of one or more other components as shown in Figure 2.1 which illustrate the membrane separation principle. Besides that, membranes can selectivity separate components over an extensive range of particle sizes and molecular weights, from macromolecular materials such as starch and protein to monovalent ions. Economically, membranes have accepted as an important place in chemical technology and are used in a wide range of applications.

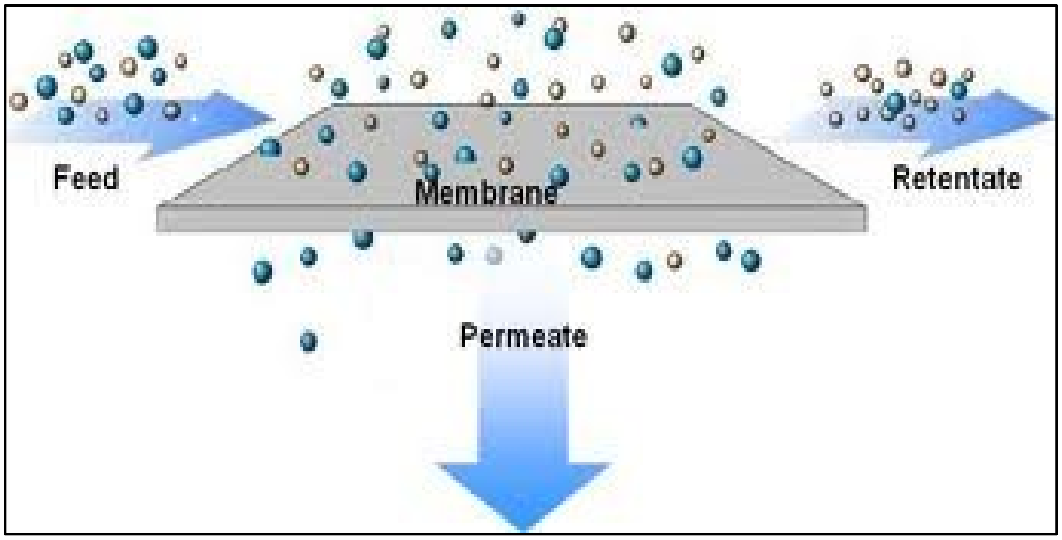

Figure 2.1: Illustrate the Membrane Separation's Principle

Indeed, membrane media is the determining component of a diffuser. It controls the operating and long term performance capabilities of the diffuser, allowing operation at a reasonable head loss and release of fine, discrete gas bubbles. Proper membrane material selection is critical in achieving desired results. Polymeric compounds are selected and engineered to produce desired surface properties, material stability, as well as environmental and chemical resistance. Then, optimum performance of a flexible membrane often directly correlates with proper membrane compound selection. On other word, improvement and advances in membrane technology have been expanding in many industrial sector; chemical, petrochemical, mineral and metallurgical, food, biotechnology, pharmaceutical, electronics, paper, pulp and water and many more applications.

2.2 Classification of Membrane Separation Processes

Membrane separations are in competition with physical methods of separation such as selective adsorption, absorption, solvent extraction, distillation, crystallization and cryogenic gas separation. Transport of selected species through the membrane is achieved by applying a driving force across the membrane. This gives a broad classification of membrane separations in the way or mechanism by which material is transported across a membrane. The flow of material across a membrane has to be kinetically driven, by the application of mechanical, chemical or electrical work (Hughes and Scott, 1996).

Certainly, membrane structure can be classified into two types which are symmetric and asymmetric ones. The functional of the membrane will depend on its structure and it is slightly different in term of physical and chemical properties as this essentially determines the mechanism of separation and thus the application.

2.2.1 Symmetric Membrane

Symmetric membrane is defined as a uniform structure which having the same chemical and physical structure throughout the hole and also called as an isotropic membrane. Generally, there are three types of symmetric membranes which are with cylindrical pores, porous and non-porous. Figure 2.2 show the schematic illustration of symmetrical membrane for microporous and nonporous dense structure.

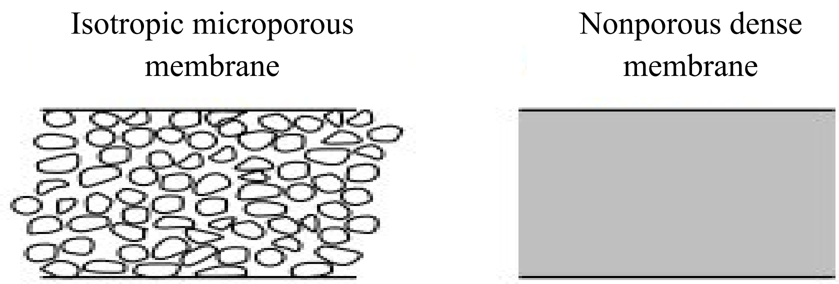

Figure 2.2: Schematic Illustration of symmetrical Membrane

2.2.1.1 Microporous

Microporous membranes are the simplest of all the symmetric membranes in term of operation. They are primarily used in filtration process. Micro porous membranes have defined pores or hole and separation is achieved by a sieving action (Hughes and Scott, 1996).

2.2.1.2 Nonporous

Nonporous mostly used in membrane separations involving molecules of the same size, gases and liquids. A driving force will take an action for diffusion through the membrane to occur. Usually, this membrane is used for gas separation.

2.2.1.3 Electrical charged

Electrically charged membranes can be dense or micro porous, however are most commonly very finely micro porous, with the pore walls carrying fixed positively or negatively charged ions. A membrane with fixed positively charged ions is known as an anion- exchange membrane and a membrane containing fixed negatively charged ions is called a cation-exchange membrane.

2.2.2 Asymmetric Membrane

Asymmetric membranes are characterized by non-uniform structure consisting of an active top layer supported by a porous sub layer. Asymmetric membranes are produced either by phase inversion from single polymers or as composite structure. Significantly, asymmetric membranes are classed as diffusion membranes and are used in reverse osmosis, gas permeation and pervaporation (Hughes and Scott, 1996). Figure 2.3 demonstrate the schematic illustration of asymmetric membrane.

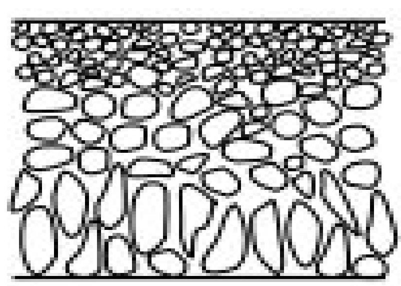

Figure 2.3: Schematic Illustration of Asymmetric Membrane

2.2.2.1 Thin film Composite Membrane

Thin film composite membrane was developed as an alternative means of producing a thin separating layer on top of a more porous support layer. The advantage of the (TFC) is that the role of the active, separating layer and the support can be separated, and each part made from optimum polymer, rather than relying upon a single polymer to provide both good separating characteristics and mechanical strength (Naylor, 1996). Figure 2.4 show the schematic demonstration of TFC membrane.

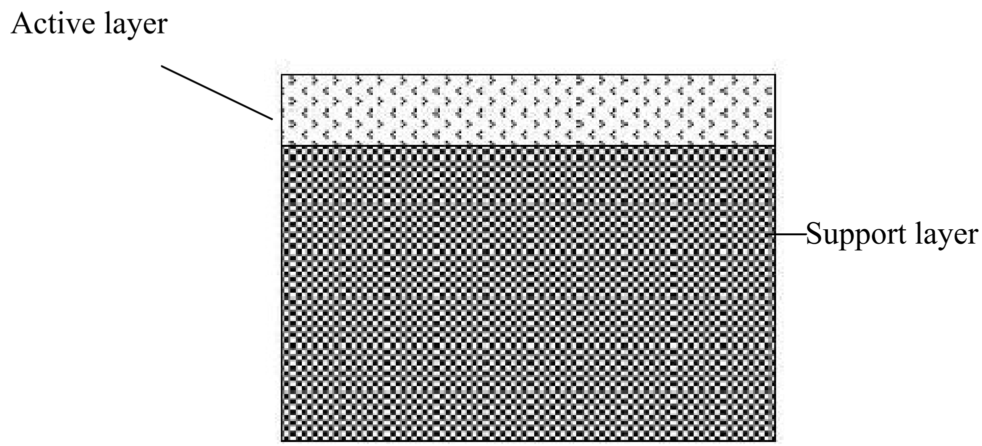

Figure 2.4: Schematic Illustration of Thin Film Composite Membrane

2.2.2.2 Liquid Membrane

Liquid membranes is a membrane which containing carriers to facilitate selective support for gases or ions. The mobile carriers which held by capillary action in the pores of a microporous film can be employed to improve single bulk material properties.

2.3 Membrane Module

Significantly, large surface areas are required for industrial applications of membrane processes. Therefore, a practical solution for providing this large surface area is packing the membranes into small unit is called as module. The module is the base for membrane process design and installation. During the process, a stream feed enters the module with a specific content at a specific flow rate. There are two streams which separate the feed stream when passing through the membrane module which are a retentate stream and permeate stream. The retentate stream is the part which retains in the feed stream while the permeate stream is the part that passes through the membrane. Typically, plate and frame module, spiral-wound module, tubular module and hollow-fiber module are largely used for industrial application.

2.3.1 Plate and Frame Module

The structure is simple where the arrangement placed in a sandwich-like fashion with their feed sides facing each other. The membrane permeate is collected from each support plate. The spacer surface is made uneven in order to promote turbulence of the feed fluid and minimize concentration polarization. The module diameter is about 20-30cm. The total membrane area in one module is up to $19m^2$, depending of the height of the module (Wang et al, 2006). Figure 2.5 shows the structure of plate and frame membrane module.

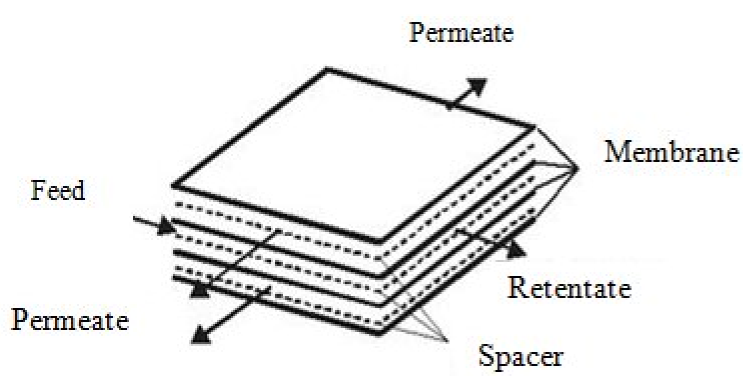

Figure 2.5: The Structure of Plate and Frame Membrane Module (technologyreport.mecadi.com)